

Nanolithographic Patterning of Catalysts for Synthesis of Carbon Nanotubes

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ABSTRACT

A novel process was developed for synthesis of carbon nanotubes (CNT) which does not require the traditional Chemical Vapor Deposition (CVD) synthesis techniques. Catalyst precursors were deposited in bulk using a “wet process” on the MEMS enabled micro-heater elements. The microheaters were coated with a layer of fullerene apriori (of 150 nm thickness) using Physical Vapor Deposition (PVD). The chip was then heated using integrated microheaters and external heaters in an inert atmosphere to obtain CNT. Thus, in this process we obviate the Chemical Vapor Deposition (CVD) process for synthesis of CNT (SWCNT and MWCNT). This work also proves the feasibility for a portable hand held instrument for synthesis of CNT “on demand”.

Keywords: Carbon nanotubes, Dip Pen Nanolithography, MEMS, Nanotechnology, Raman spectroscopy.

1 INTRODUCTION

Carbon nanotubes (CNT) were discovered by Ijima using the arc-discharge process in 1991 [1], and since then, various techniques have been devised to synthesize carbon nanotubes. CNT are considered for various applications owing to their novel mechanical [2] and electronic properties [3]. Processes like Chemical Vapor Deposition or “CVD” [4], and the HiPCo process [5] were developed and optimized subsequently. Mass production of nanotubes would allow their commercial use [6]. Furthermore if the synthesis process can be controlled so as to have a desired type of nanotubes with controlled diameters, properties of nanotubes could be even more exploited.

This work is an extension of our earlier investigation for using Dip Pen Nanolithography (DPN) techniques [7-9] for the synthesis of CNT and controlling the chirality of the synthesized CNT [10-12]. In this paper, we try to present a refined process for the synthesis, which overcomes some of the hurdles mentioned in the commercial processes described above.

2 EXPERIMENTAL APPARATUS

Custom designed MEMS (Micro Electro Mechanical Systems) platforms were used for the synthesis process for carbon nanotubes (the MEMS substrates were fabricated by MEMS Exchange Inc.). VA. These platforms were in the form of square chips. The dimension of the substrate was 3.5 x 3.5 x 0.5 mm. Three types of serpentine heaters were designed for the substrate. Titanium was used as the material for the heater. Three different types of heaters with

variation in length and orientation were used on the substrate. The lengths of the microheaters are 18 mm, 19 mm and 42 mm. The thickness of the heater elements is 100nm.

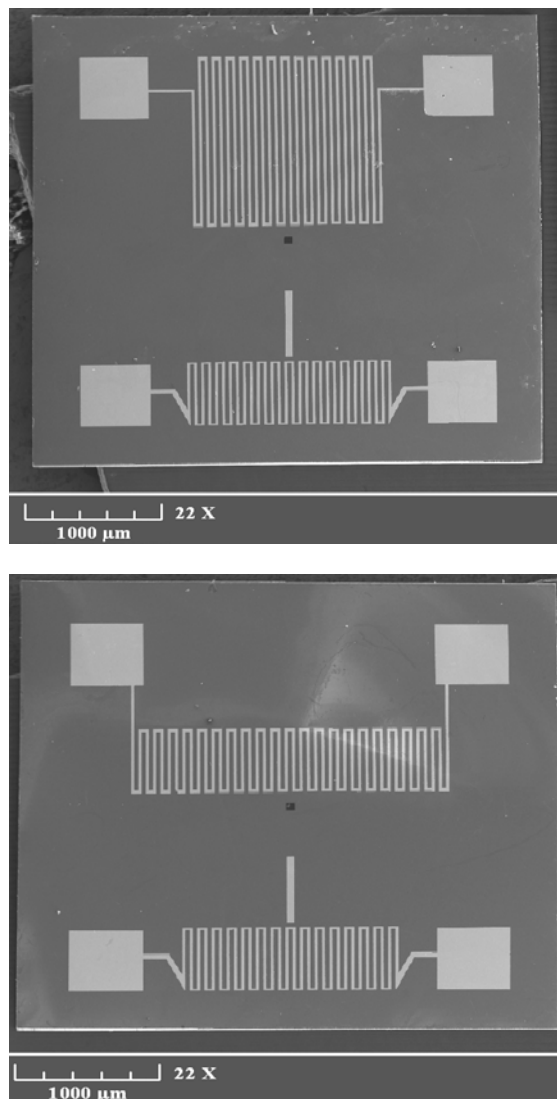


Figure 1. Scanning Electron Microscopy (SEM) images of the two types of substrates used in the synthesis of Carbon Nanotubes (CNT). There are three different types of micro-heaters microfabricated insitu on the silicon nitride membrane, a backside square opening etched in silicon for exposing the membrane at the center, and a vertical alignment marker (gold) perpendicular to the heater aligned with the membrane.

Two types of MEMS platforms (substrates) were fabricated for the synthesis of the CNT, with each substrate

having two heaters on either edge of the top side. A silicon nitride membrane was deposited on the top side in the middle portion of the silicon chip. The membrane had a back side opening of 60 μm x 60 μm square. A metal pad was deposited near the edge of the square membrane and perpendicular to the heaters - using "lift-off" process to serve as an 'alignment mark'. The chip structure is shown in **Figure 1**.

The Mbraun Labmaster double glove box system with gas purification (located at the Center for Nanomanufacturing, University of Texas, Austin); was used for the vapor deposition of fullerene layer on this chips. This instrument consists of a two chamber glove box system. A spin coater (specialty coating systems model P6700) is available inside the smaller glove box chamber. An Edwards's thermal deposition chamber with four sources is available inside the larger glove box. A vacuum oven is mounted at one end of the glove box. Multiple chips are mounted on a glass slide with a double sided tape, and this glass slide is placed inverted on the roof of in the thermal deposition chamber. Fullerene powder (Manufactured by Nano-C Inc., Westwood, MA) was placed in the target container on the chambers base. The container was electrically heated at a pressure of 1 mTorr to a temperature of 550 $^{\circ}\text{C}$ to enable sublimation of the fullerene powder. The deposition rate by sublimation was estimated to be 20 nm/s for a total deposition time of 10 s. The fullerene thickness was estimated to be 150 nm at the end of the vapor deposition process using a profilometer.

Metal catalysts (Nickel chloride, Cobalt Chloride, Palladium Chloride) were prepared by mixing the solid powder into water with minimal heating for uniformity. Sodium Hydroxide was used in the preparation of the PdCl_2 , since it doesn't form a direct solution with water. A digital DC power supply with enough power rating is used, which has displays for monitoring the current and voltage. A wire thermocouple is used to measure the temperature, with the welded end on the chip and the open end connected to a thermocouple reader.

MINCO mica external heaters were used to raise the temperature of the coated substrates in the CNT synthesis experiments. Suspended in mid-air Individual heaters can be heated to temperatures of around 200 $^{\circ}\text{C}$, So three heaters were mounted together, stacked above each other and connected electrically in parallel. The heater assembly was used to heat the chips to 550 $^{\circ}\text{C}$, required for the synthesis process.

A dessicator is used as the chamber for the synthesis process. The dessicator has two openings. One of this is connected to a Nitrogen tank and the other serves as an inlet for the electrical connections. The external heaters, Chips, and the thermocouples are placed in the dessicator, 2 alligator pin clamps are used for suspending the heaters and positioning the thermocouple. Also a humidity sensor is positioned inside the dessicator.

3 EXPERIMENTAL PROCEDURE

It has been demonstrated experimentally that Carbon Nanotubes (CNT) can be synthesized with Fullerene as the source for carbon, where the synthesis temperature is $\sim 500^{\circ}\text{C}$ [13]. Metal catalysts also play a significant role in the formation of carbon nanotubes. The catalyst particles serve as nucleation sites for formation of CNT from fullerene [14]. Nickel Chloride, Cobalt Chloride, and Palladium chloride were used as catalyst precursors in this experiment. These precursors were prepared in an aqueous solution as mentioned above. Each catalyst was deposited as a bulk layer on separate fullerene coated chips with the aid of a syringe. The catalyst precursor solution allowed to dry at room temperature after dispensing it on the fullerene coated chips.

In an initial attempt, heater connections were made across the bond-pads of one of the heater per chip. The connections were possible with normal electrical wires available commercially with very small diameters, in accordance with the bond-pad areas. The apparatus was placed in a dessicator and connected to nitrogen supply from a pressurized cylinder. The experiments were performed in an inert atmosphere by passing the nitrogen into the dessicator. A humidity sensor was also placed inside the dessicator. The relative humidity in the air was 38.2% at the beginning before passing nitrogen gas. After a duration of 20 minutes, the humidity was found to be 3.8% inside the dessicator. At this stage, current was passed through the microheaters in the chip. However, the chips were damaged when they reached a temperature of $\sim 300^{\circ}\text{C}$ due to stress concentration. Since this temperature was not suitable enough for CNT synthesis, external MINCO heaters were therefore used in this process. The external heaters connected in a parallel assembly as discussed above. The chips were then placed on the MINCO heater assembly for direct contact heating. The temperature of the heaters was then raised slowly in steps of 10 $^{\circ}\text{C}$ per minute until the temperature reached 510 $^{\circ}\text{C}$. It has been reported that lower synthesis temperatures yield a tighter distribution of the diameters (and correspondingly the chirality) of the synthesized CNT [15]. The heater assembly was maintained at this temperature for 15 minutes and the power supply was then cutoff, along with the flow of nitrogen. The characterization of these samples was then carried out using Raman Spectroscopy and Scanning Electron Microscopy.

4 RESULTS AND DISCUSSION

The synthesized CNT can be characterized to determine the material properties using several techniques which include SEM/ TEM, Raman spectroscopy, absorption spectroscopy, etc. SEM/TEM and Raman spectroscopy are widely used for their convenience and ease. Imaging techniques (which includes SEM and TEM) provides a direct visual observation. Raman spectroscopy provides distinct information of the vibrational modes

which are detected using peaks in known Raman shifts in wavenumber. These peaks are seen at three locations, first being the Graphite Peak (G-Peak) around 1600 cm^{-1} , second, Defect Peak (D-Peak) around 1350 cm^{-1} , and third, the Radial Breathing Modes ($100\text{-}300\text{ cm}^{-1}$). RBM peaks are caused by the vibration along the radial direction of the individual CNT, and are widely used to obtain information about the distribution of the diameters of the synthesized single walled CNT (SWCNT) [16]. When the samples were excited by $633\text{ }\mu\text{m}$ laser, after the experiment (Model: LabRam IR Confocal Raman Spectroscopy - Microscopy Instrument, Manufacturer: JY Horiba, Japan), the above mentioned peaks in RBM, G and D bands were distinctly visible for the experiments using Palladium catalyst. **Figure 2** shows the obtained Raman spectra.

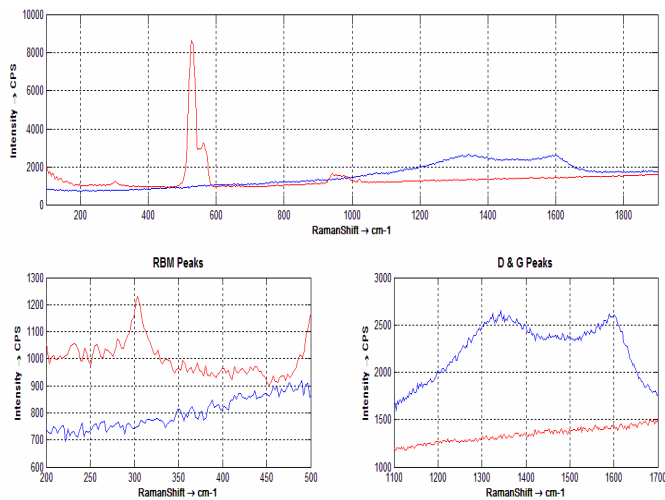


Figure 2: The Raman spectra of the sample before (in Red) and after (in Blue) the synthesis of CNT from Fullerene coated chips.

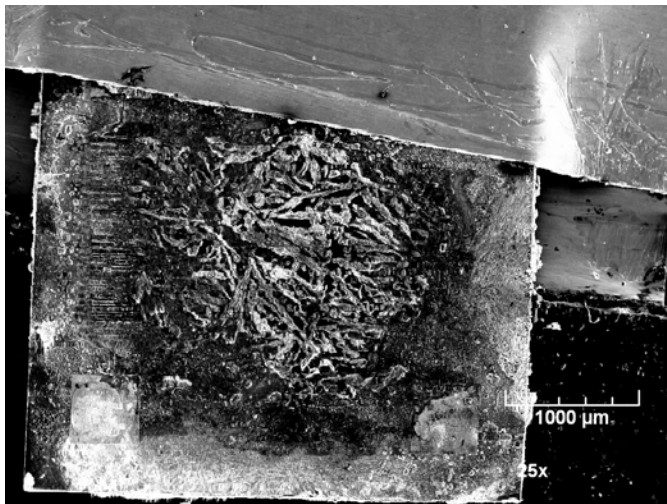


Figure 3: Image of the PdCl₂ bulk deposited sample. Conductive copper tape used for mounting the sample is observed at the top. The conductive tape is used to minimize the effects of charge trapping.

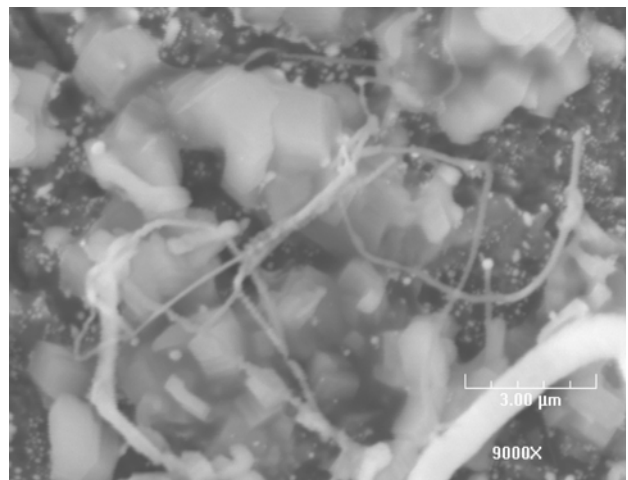
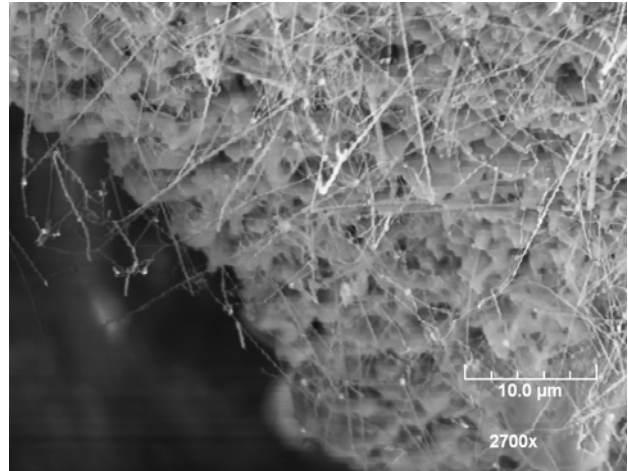


Figure 4: Top: The synthesized Carbon Nanotubes (CNT) are observed on the edge of the MEMS chip. Bottom: Image obtained at a higher magnification shown the synthesis experiment yields carbon nanotube bundles (SWCNT and MWCNT) and carbon nanofibers which are estimated to be 20-200 nm in diameter.

As seen from **Figure 2** the peaks at $1340\text{ }\&\text{ }1600\text{ cm}^{-1}$ are clearly visible. Since the D band is more intense, it indicates presence of multi-walled carbon nanotubes [11, 12]. The peak at 300 cm^{-1} seen in the RBM region and the peak at 520 cm^{-1} in indicative of silicon, which is the substrate material. For confirmation of the data from Raman spectra, the Palladium samples were observed using Scanning Electron Microscopy. **Figure 3** shows the over all view of the bulk deposited sample after the experiment. **Figure 4** shows that the diameters of carbon nanotubes obtained in this synthesis experiment ranged from 20 nm to 200nm. This variation of the diameter of the carbon nanotubes and the haphazard location mixed with carbon fibers was expected owing to the bulk deposition of the metal catalyst. Energy dispersive Spectroscopy (EDS) techniques were used to analyze the elemental composition of the sample. Data obtained by EDS unit (inbuilt into the SEM apparatus) is shown below in Table 1.

Table 1

Element	Weight(%)
Silicon (Si)	13.11
Palladium (Pd)	3.67
Carbon (C)	83.22
Total	100.00

5 CONCLUSION & FUTURE DIRECTION

In this work we have developed a novel process for synthesis of carbon nanotubes (CNT) without requiring the conventional synthesis techniques such as Chemical Vapor Deposition (CVD) process or the process gasses that are used in conventional synthesis techniques. CNT can be synthesized at temperatures of around 500°C. The bulk deposition of the catalyst over vapor deposited fullerene layer yields a mixture of carbon nanotubes with different diameters. By optimizing this process for catalyst deposition, with the help of techniques like Dip Pen Nanolithography, it would be possible to synthesize carbon nanotubes of a desired diameter and hence a 'specific-chirality' at desired locations.

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